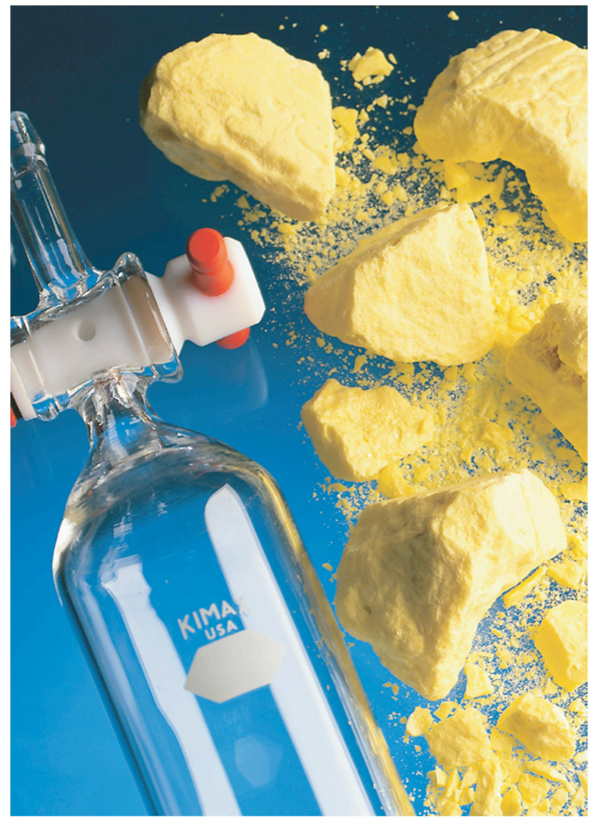
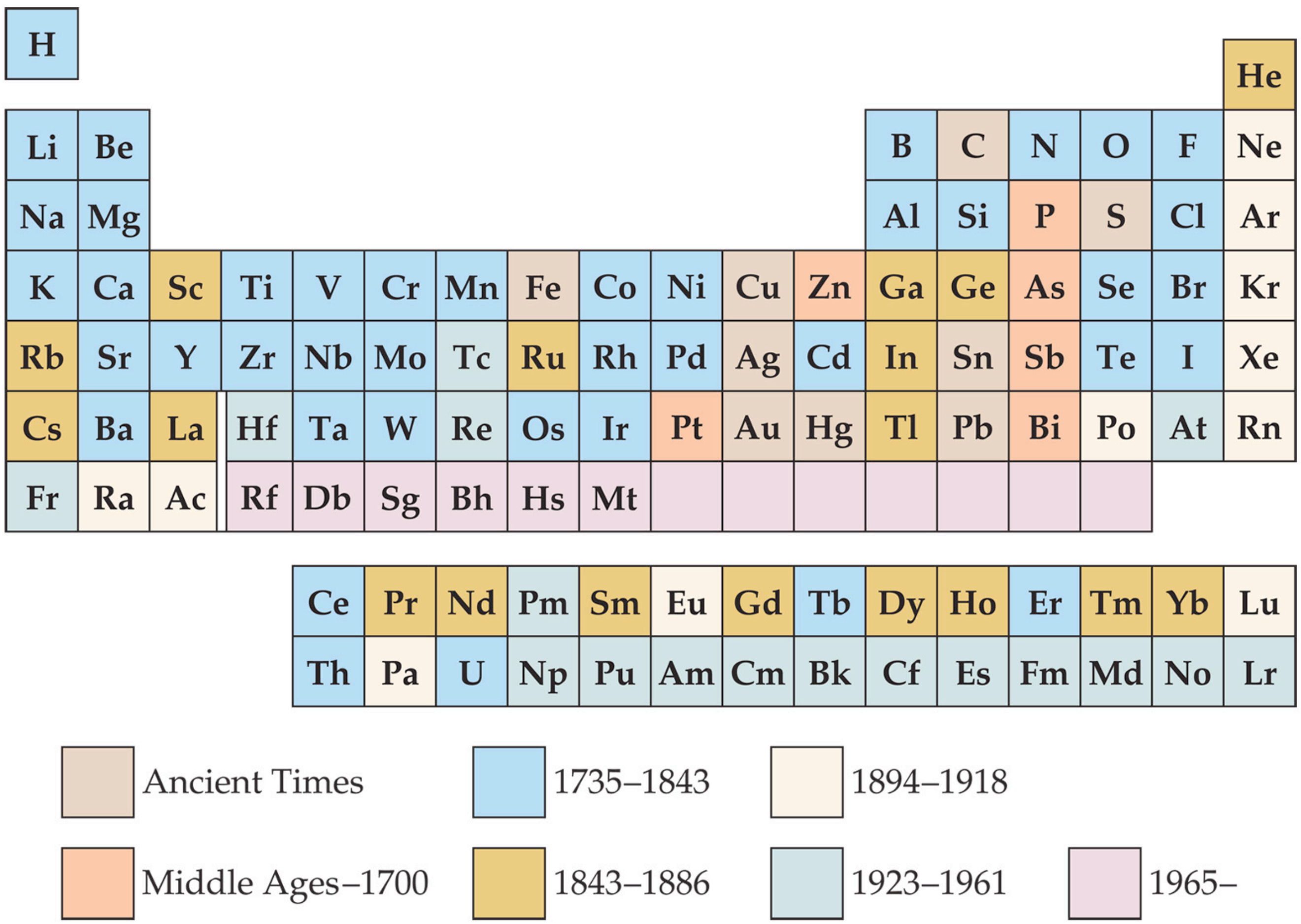
Chapter 7
Periodic Properties of the Elements

Development of Periodic Table

- Elements in the same group generally have similar chemical properties.
- Properties are not identical, however.



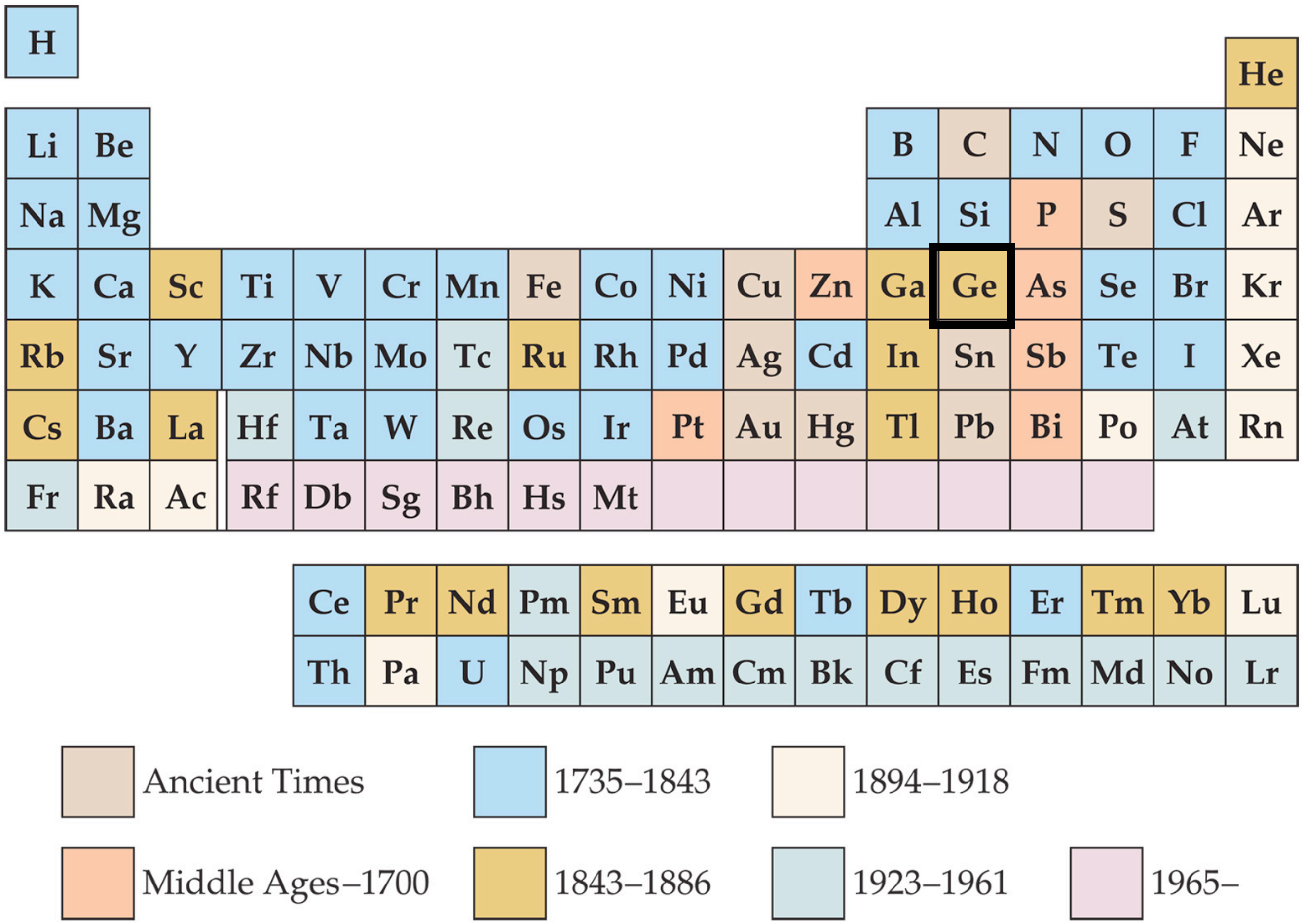
Development of Periodic Table



Dmitri Mendeleev and Lothar Meyer independently came to the same conclusion about how elements should be grouped.

Periodic Properties of the Elements

Development of Periodic Table



Mendeleev, for instance, in 1871 predicted germanium (which he called eka-silicon) to have an atomic weight between that of zinc and arsenic, but with chemical properties similar to those of silicon.

Periodic Properties of the Elements

Development of Periodic Table

Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat (J/g-k)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride (°C)	A little under 100	84

Mendeleev's prediction was on the money

But why? (Mendeleev had no clue).

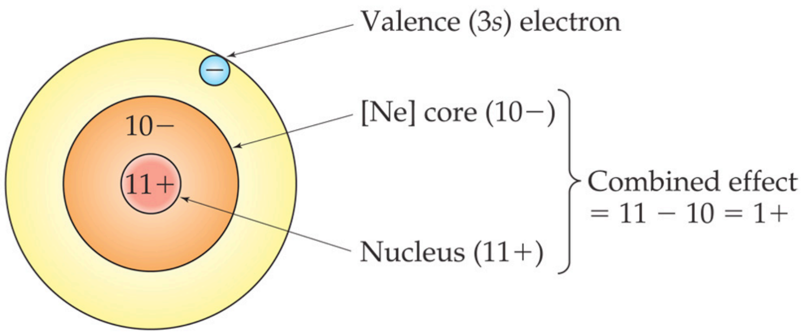
Periodic Properties of the Elements

Periodic Trends

- In this chapter we'll explain why
- We'll then rationalize observed trends in
  - Sizes of atoms and ions.
  - Ionization energy.
  - Electron affinity.

Effective Nuclear Charge

Na atom looks like this:



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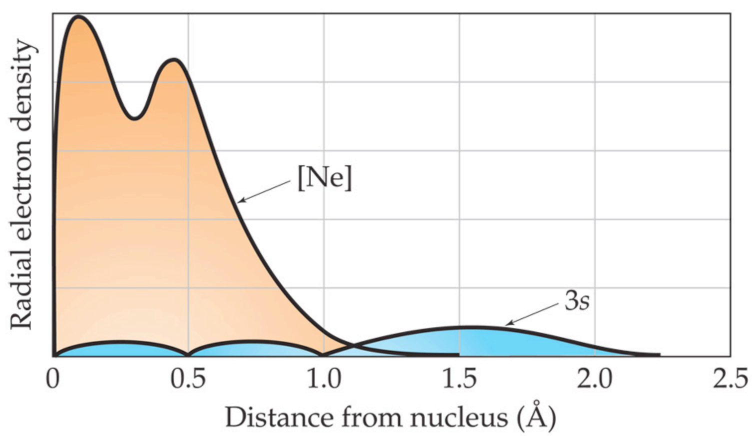
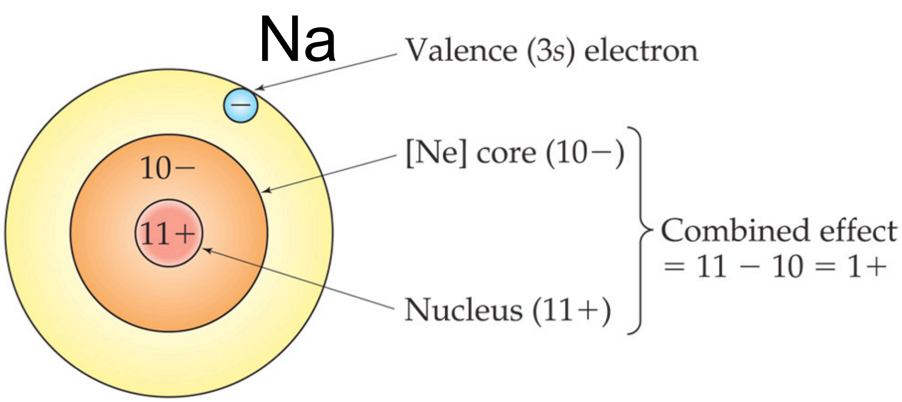


- In a many-electron atom, electrons are both attracted to the nucleus and repelled by other electrons.
- The nuclear charge that an electron "feels" depends on both factors.
- It's called Effective nuclear charge.
- electrons in lower energy levels "shield" outer electrons from positive charge of nucleus.

Effective Nuclear Charge



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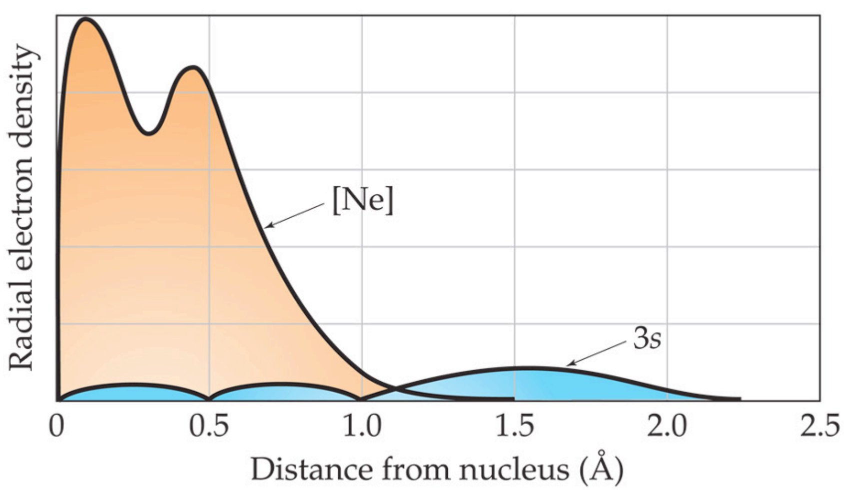

The effective nuclear charge, Z_{eff}, is:

$Z_{\mathrm{eff}} = Z - S$

Where:

Z = atomic number

S = screening constant, usually close to the number of inner (n-1) electrons.

Effective Nuclear Charge

- Example: Which element’s outer shell or “valence” electrons is predicted to have the largest Effective nuclear charge?   Kr, Cl or O?

Effective Nuclear Charge

- Example: Which element's outer shell or "valence" electrons is predicted to have the largest Effective nuclear charge? Kr, Cl or O?

- Cl: $Z_{eff} \approx 17 - 10 = 7$
- O: $Z_{eff} \approx 8 - 2 = 6$
- N: $Z_{eff} \approx 7 - 2 = 5$
- Ca: $Z_{eff} \approx 20 - 18 = 2$

Valence electrons

Many chemical properties depend on the valence electrons.

Valence electrons: The outer electrons, that are involved in bonding and most other chemical changes of elements.

Rules for defining valence electrons.

1. In outer most energy level (or levels)
2. For main group (representative) elements (elements in s world or p world) electrons in filled d or f shells are not valence electrons
3. For transition metals, electrons in full f shells are not valence electrons.

Periodic Properties of the Elements

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Examples: (valence electrons in blue)

P: [Ne]$3s^2 3p^3$

As: [Ar] $4s^2 3d^{10} 4p3$

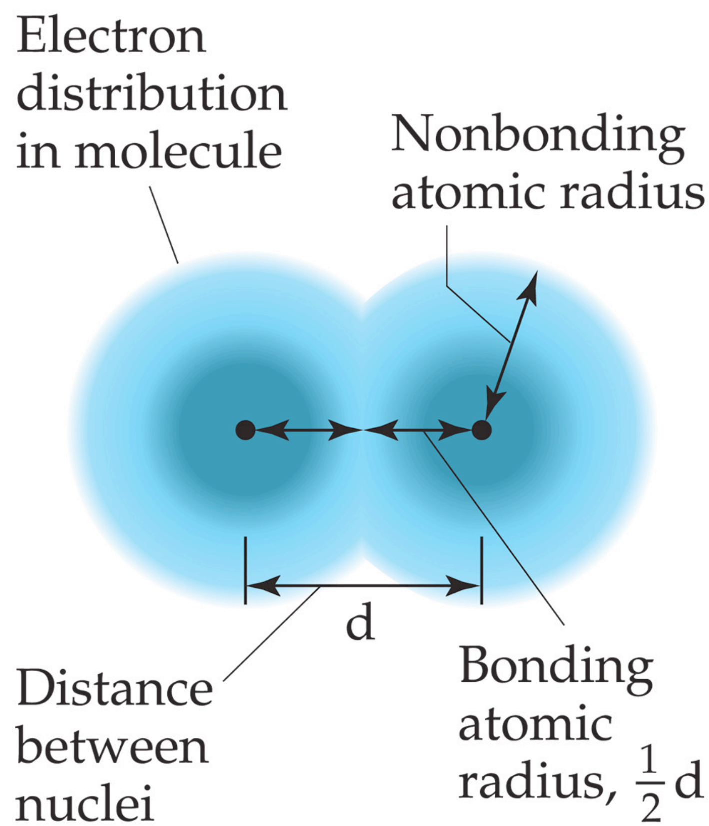
I: [Kr]$5s^2 4d^{10} 5p^5$

Ta: [Kr]$6s^2 4f^{14} 5d^3$

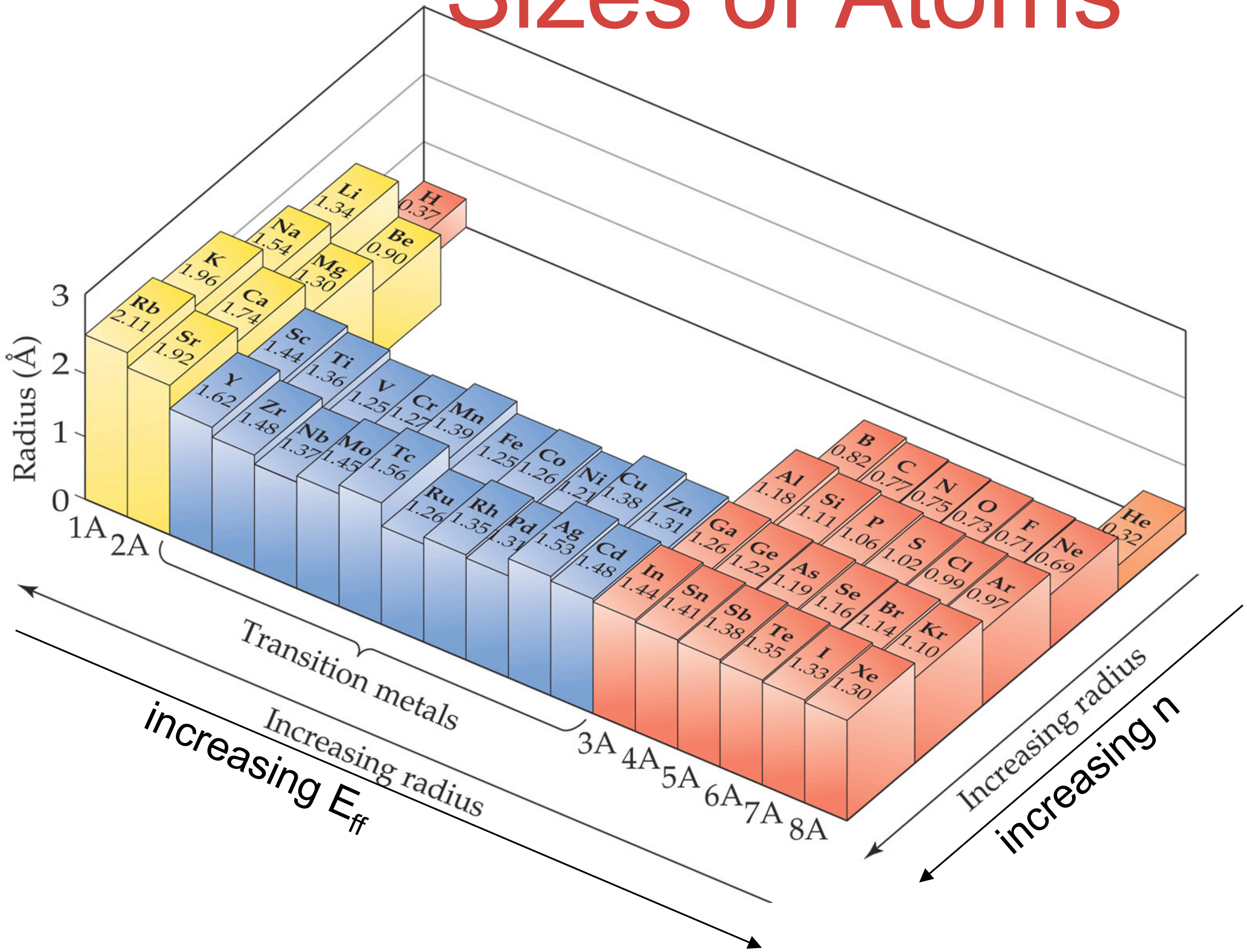
Zn: [Ar]$4s^2 3d^{10}$

Sizes of Atoms

The bonding atomic radius is defined as one-half of the distance between covalently bonded nuclei.



Sizes of Atoms



Bonding atomic radius tends to…

…decrease from left to right across a row due to increasing Z_{eff}.

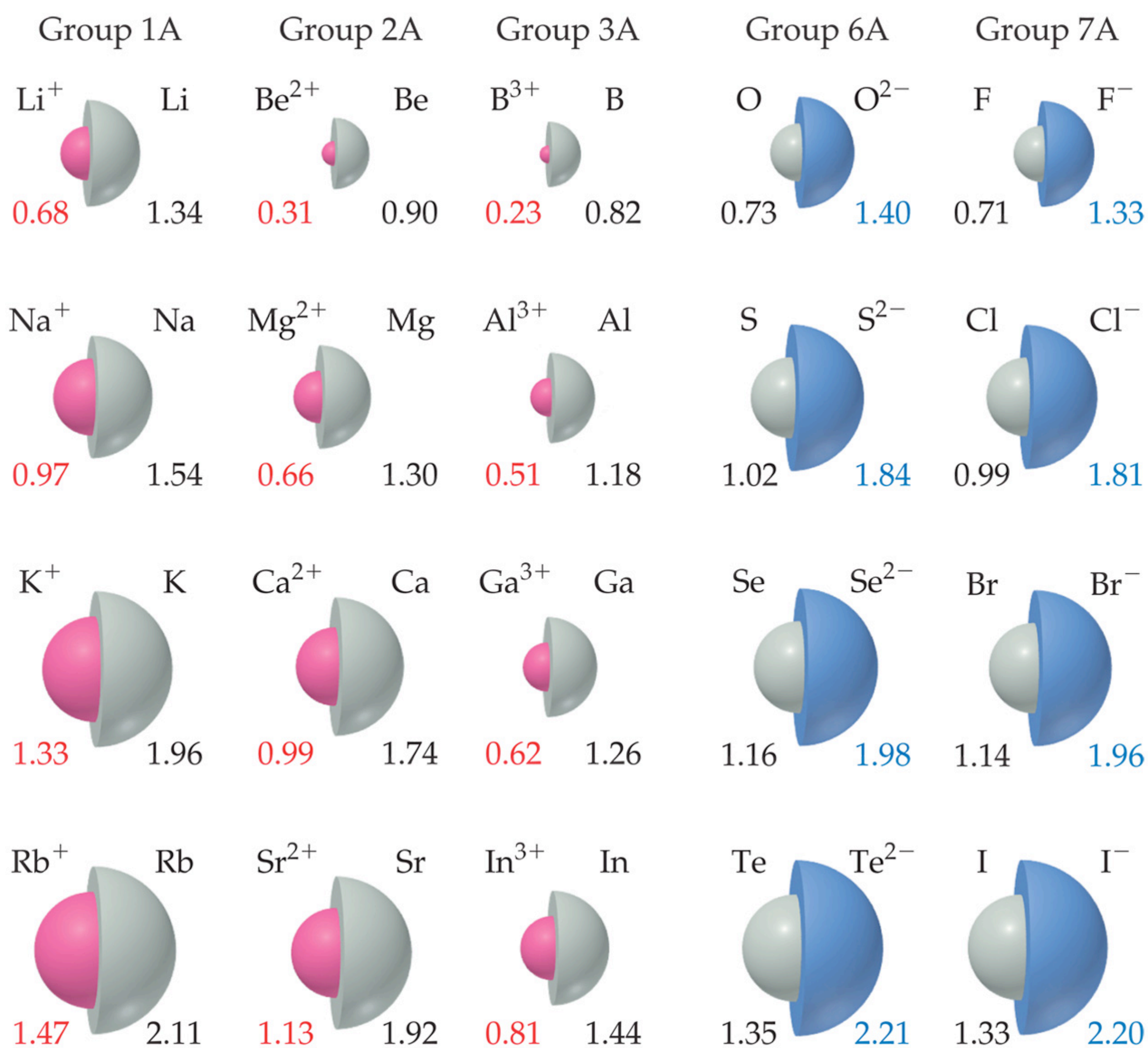
…increase from top to bottom of a column due to increasing value of *n*

Periodic Properties of the Elements

Exams are being graded now but aren’t finished.
We may have them by the end of today.

My T.A.s had to sacrifice bunnys for science.

Sizes of Ions

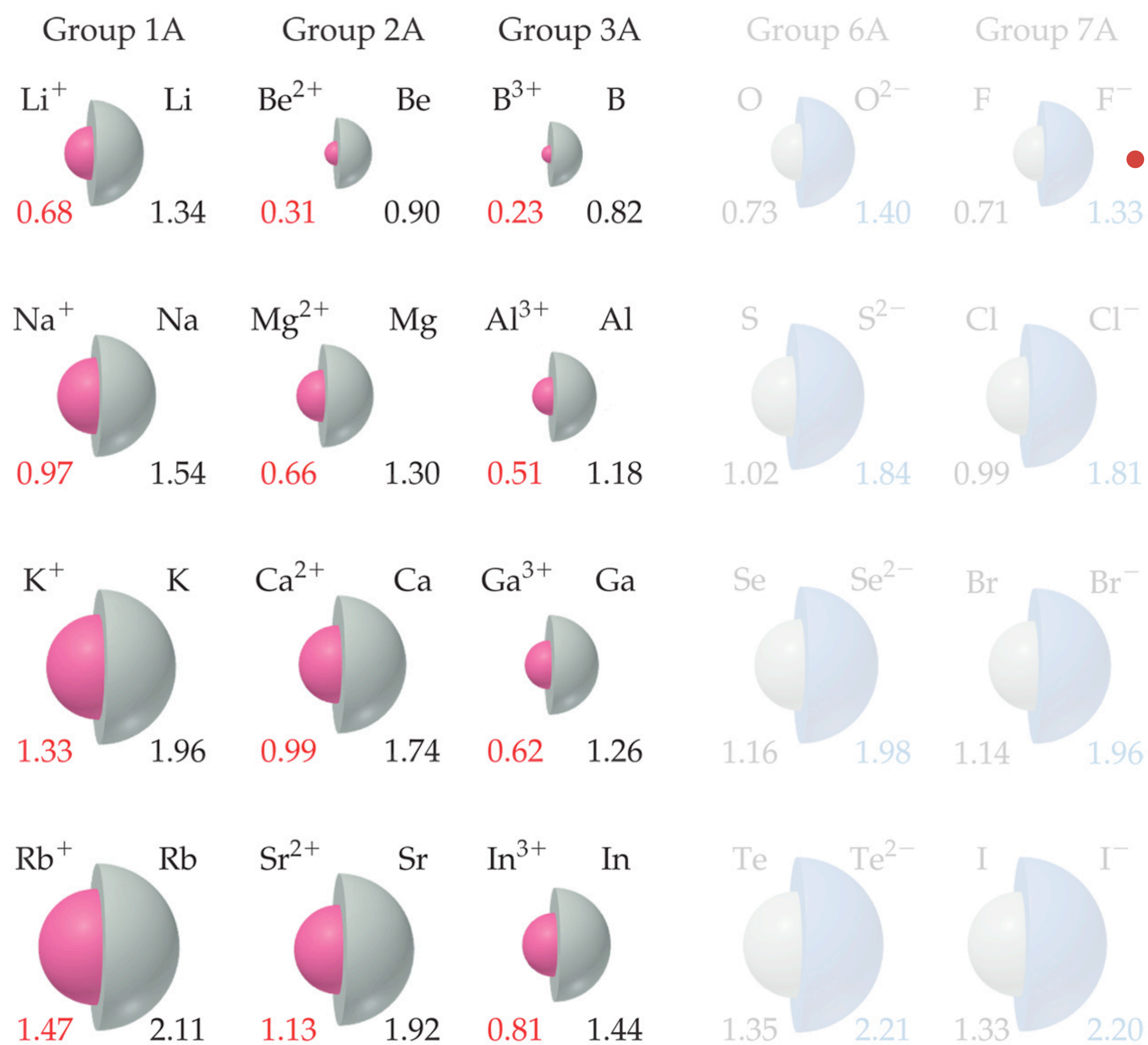


Ionic size depends upon:

- Nuclear charge.
- Number of electrons.
- Orbitals in which electrons reside.

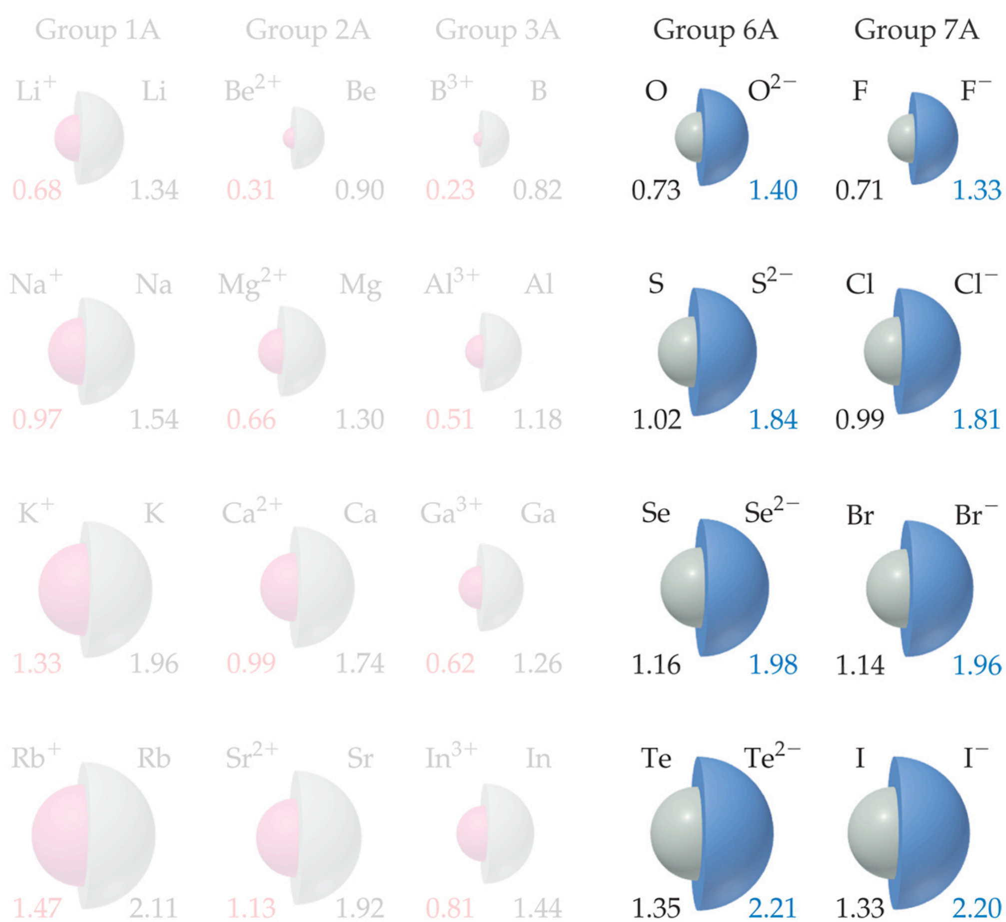
Periodic Properties of the Elements

Sizes of Ions



- Cations are smaller than their parent atoms.
  - ➢ The outermost electron is removed and repulsions are reduced.

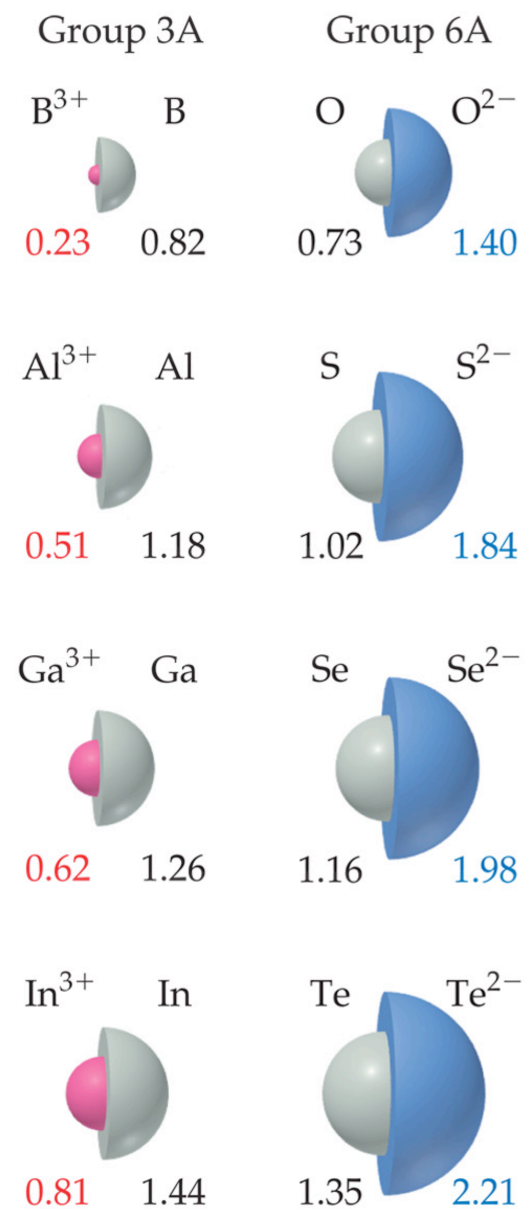
Sizes of Ions



- Anions are larger than their parent atoms.
  - Electrons are added and repulsions are increased.

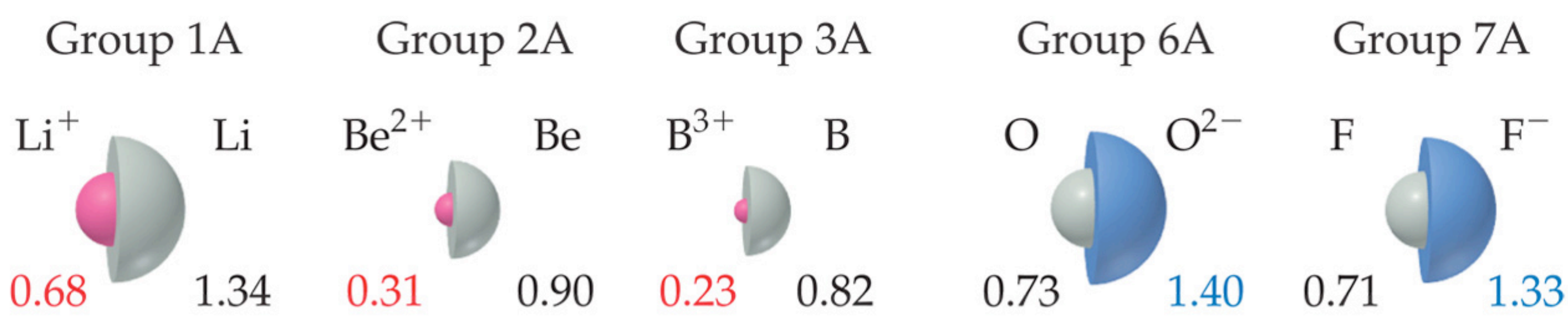
Sizes of Ions

- Ions increase in size as you go down a column.
  - Due to increasing value of *n*.



Sizes of Ions

- In an isoelectronic series, ions have the same number of electrons.
- Ionic size decreases with an increasing nuclear charge.



Periodic Properties of the Elements

atom/ion size examples

- Put the following in order of size, smallest to largest:

- Na, Na^{+}, Mg, Mg^{2+}, Al, Al^{3+}, S, S^{2-}, Cl, Cl^{-}

Atom size examples

Al^{3+}, Mg^{2+}, Na^{+}, Cl, S, Al, Mg, Na, Cl^{-}, S^{2-}

Start with atoms with no n=3 electrons, order isoelectronic by nuclear charge.

Next, neutral atoms highest E_{ff} first

Last, anions, highest E_{ff} first

Ambiguity: anions versus neutrals (is Cl^{-} really larger than Na?)

Don’t worry about it.

Ionization Energy

- Amount of energy required to remove an electron from the ground state of a gaseous atom or ion.
  - First ionization energy is that energy required to remove first electron.
  - Second ionization energy is that energy required to remove second electron, etc.

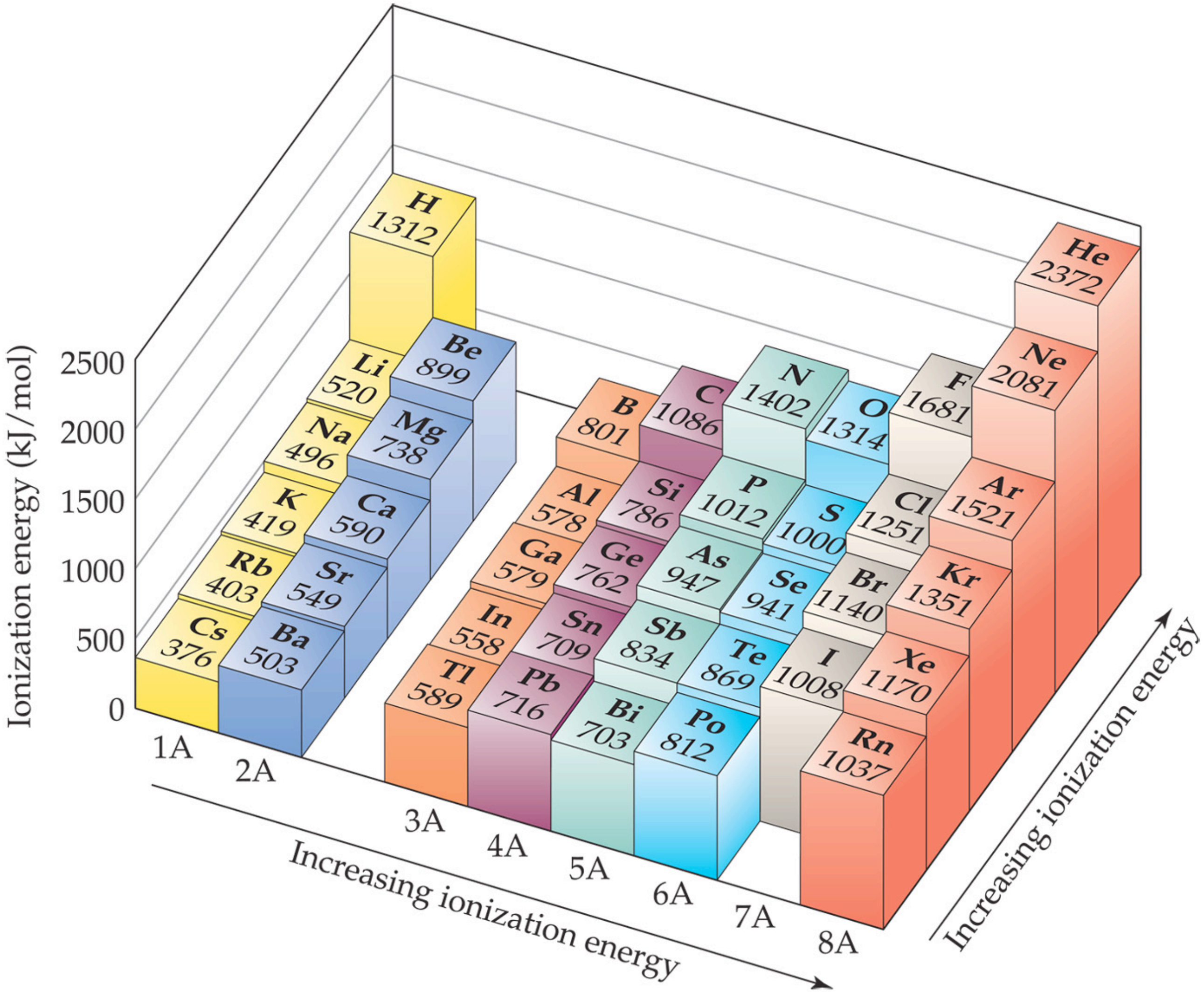
$$El \longrightarrow El^{+} + e^{-}$$
$$Na \longrightarrow Na^{+} + e^{-}$$

Ionization Energy

- It requires more energy to remove each successive electron.
- When all valence electrons have been removed, the ionization energy takes a quantum leap.

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4562			(inner-shell electrons)		
Mg	738	1451	7733				
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

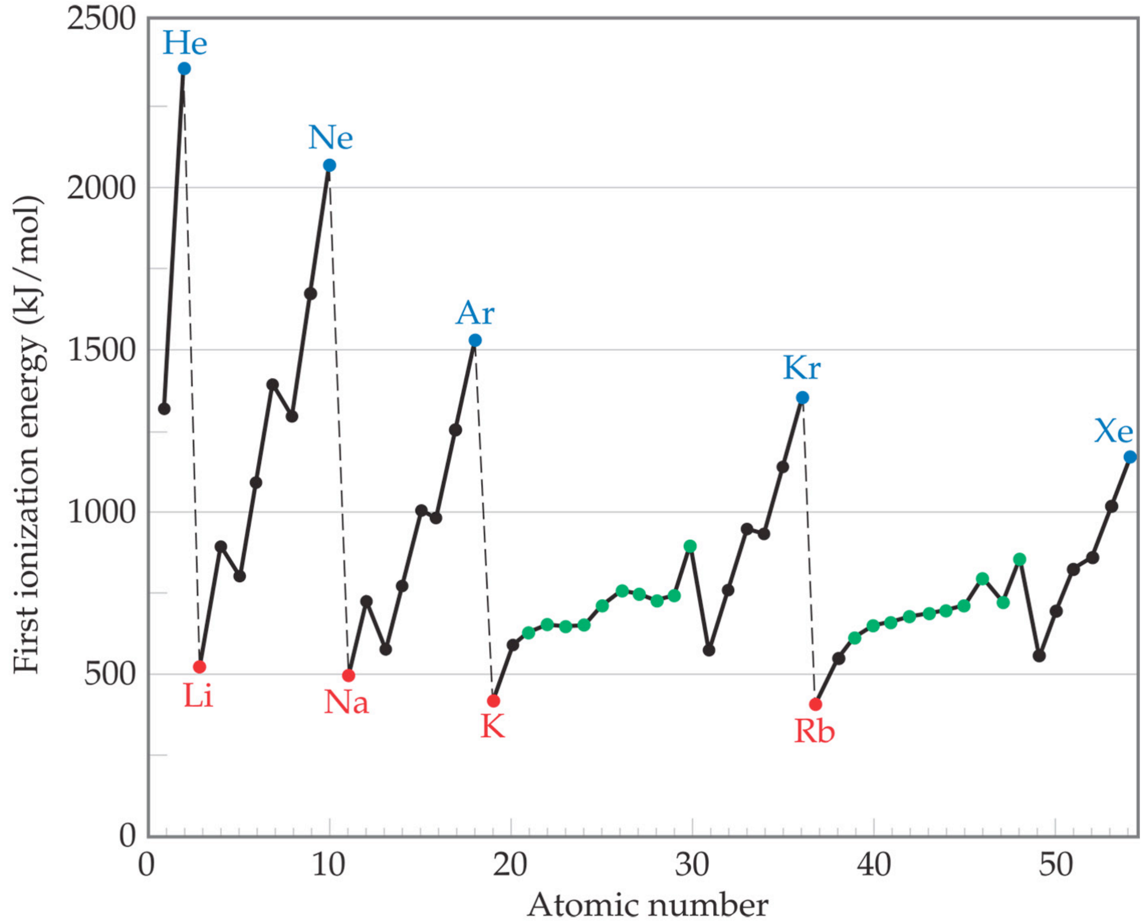
Trends in First Ionization Energies



- going down a column, less energy to remove the first electron.
  - For atoms in the same group, Z_{eff} is essentially the same, but the valence electrons are farther from the nucleus.

Trends in First Ionization Energies

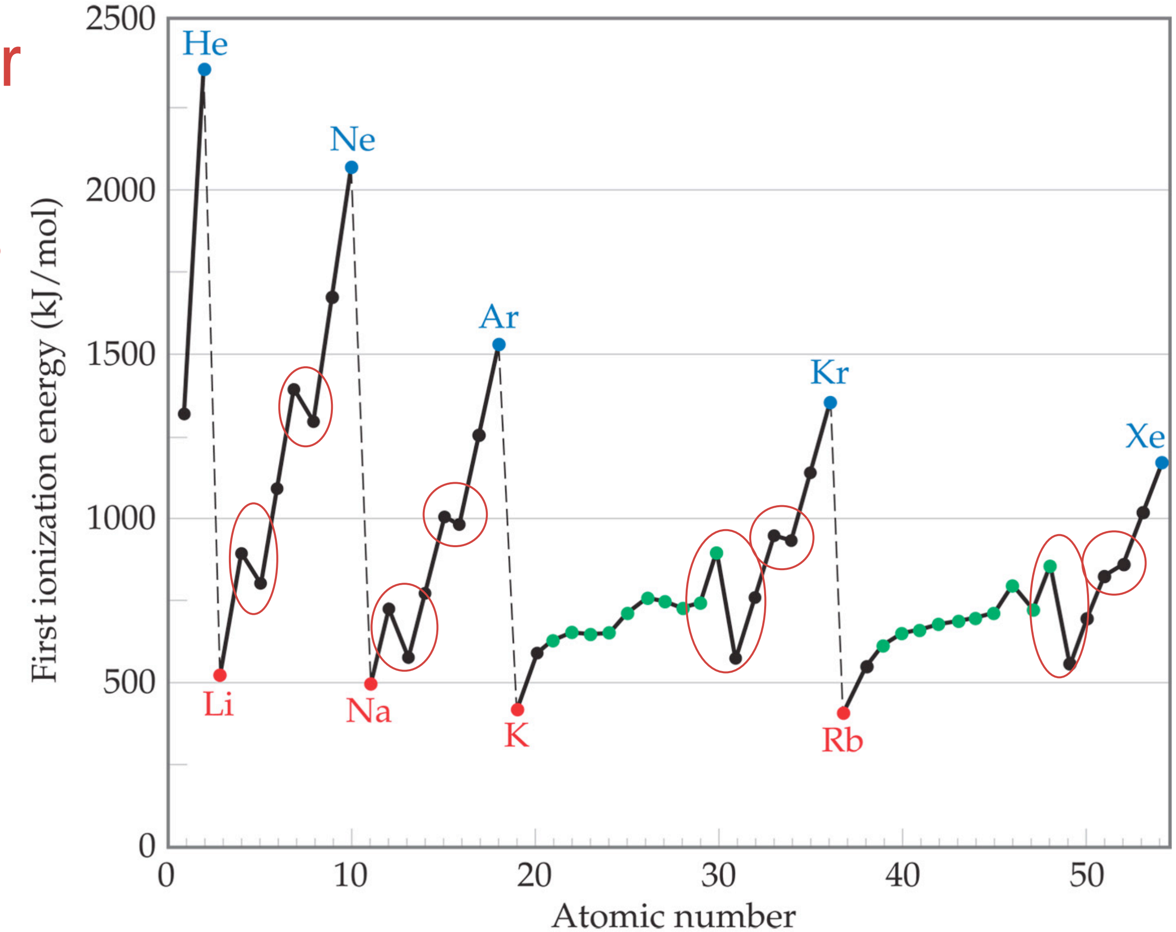
- Generally, it gets harder to remove an electron going across.
  - ➢ As you go from left to to right, Z_{eff} increases.



Properties of the Elements

Trends in First Ionization Energies

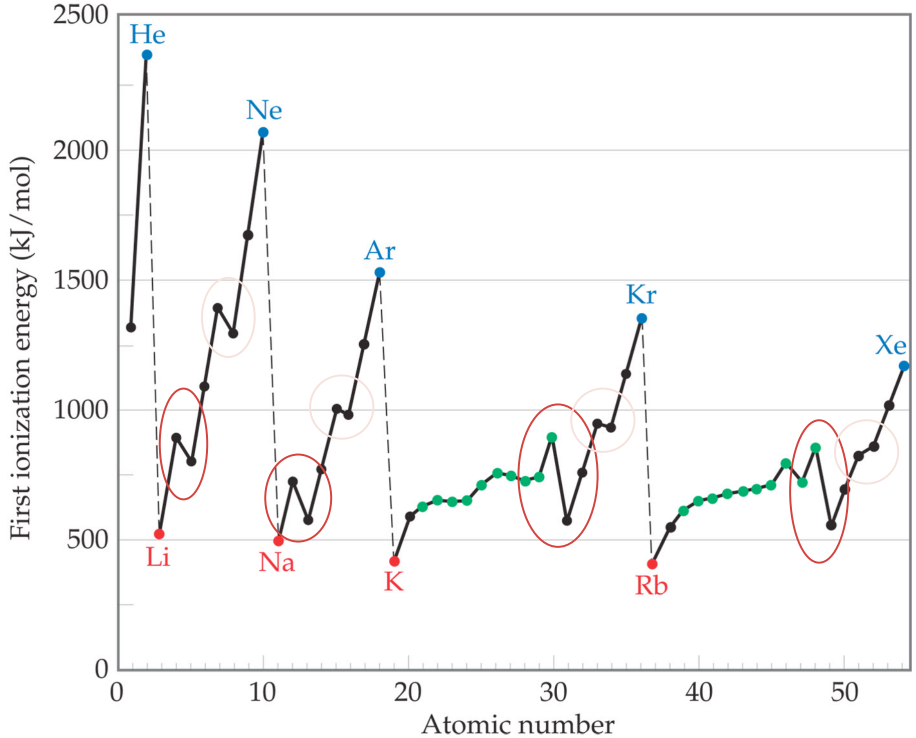
On a smaller scale, there are two jags in each line. Why?



Periodic Properties of the Elements

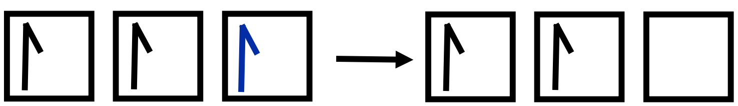
Trends in First Ionization Energies

- The first occurs between Groups IIA and IIIA.
- Electron removed from *p*-orbital rather than *s*-orbital
  - ➢ Electron farther from nucleus
  - ➢ Small amount of repulsion by *s* electrons.

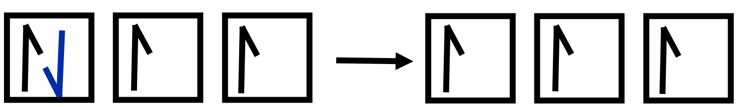


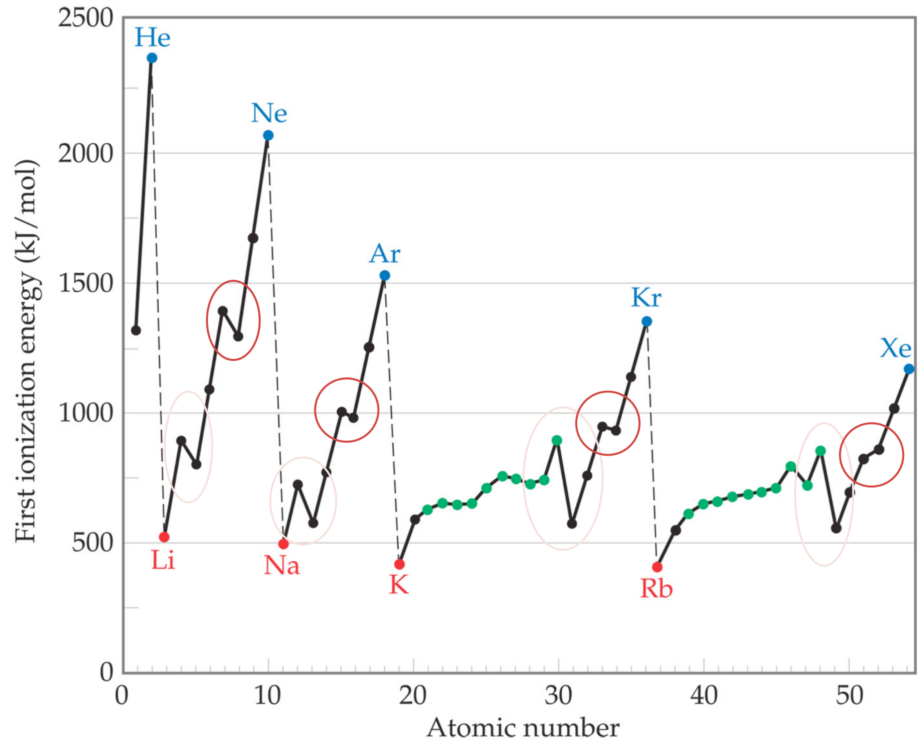
Trends in First Ionization Energies

- The second occurs between Groups VA and VIA.
  - Electron removed comes from doubly occupied orbital.
  - Repulsion from other electron in orbital helps in its removal.



versus:





Periodic Properties of the Elements

Electron Affinity

Energy change accompanying addition of electron to gaseous atom:

$$Cl + e^{-} \longrightarrow Cl^{-}$$

Trends in Electron Affinity

H −73							**He** > 0
Li −60	**Be** > 0	**B** −27	**C** −122	**N** > 0	**O** −141	**F** −328	**Ne** > 0
Na −53	**Mg** > 0	**Al** −43	**Si** −134	**P** −72	**S** −200	**Cl** −349	**Ar** > 0
K −48	**Ca** −2	**Ga** −30	**Ge** −119	**As** −78	**Se** −195	**Br** −325	**Kr** > 0
Rb −47	**Sr** −5	**In** −30	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** > 0
1A	2A	3A	4A	5A	6A	7A	8A

In general, electron affinity becomes more exothermic as you go from left to right across a row.

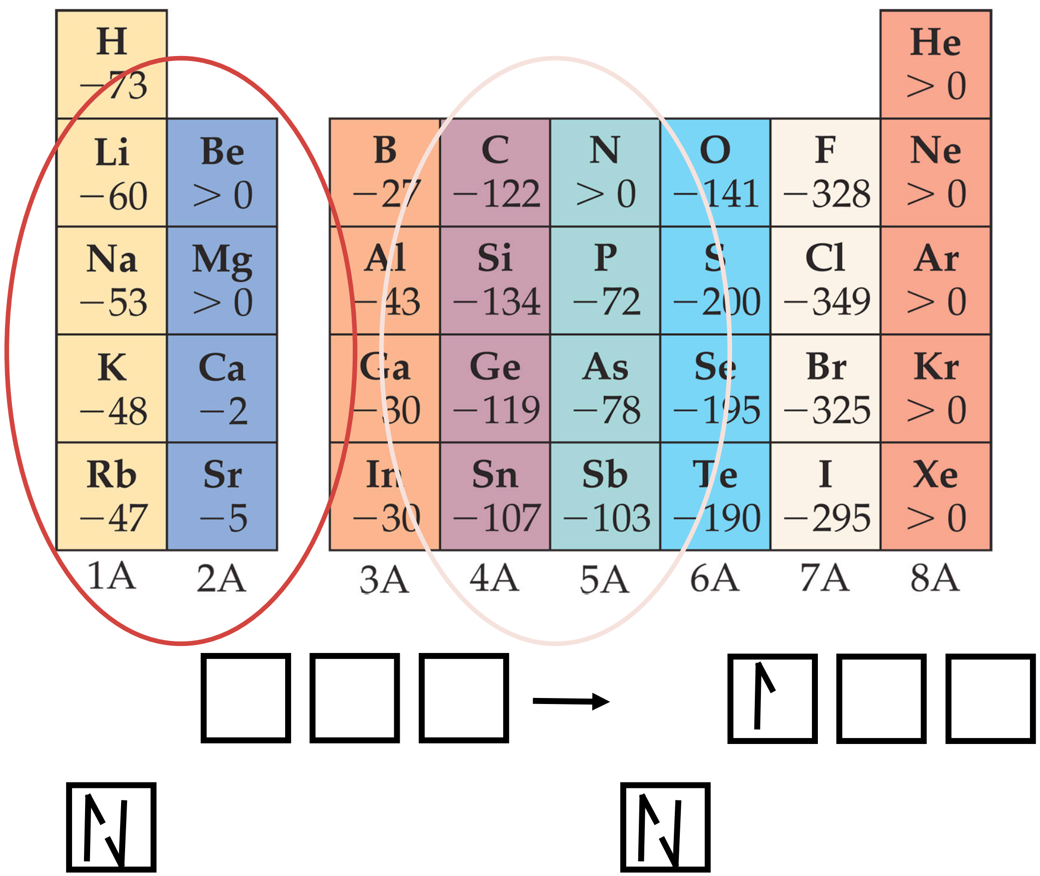
Periodic Properties of the Elements

Trends in Electron Affinity

1A	2A	3A	4A	5A	6A	7A	8A
H −73							He > 0
Li −60	Be > 0	B −27	C −122	N > 0	O −141	F −328	Ne > 0
Na −53	Mg > 0	Al −43	Si −134	P −72	S −200	Cl −349	Ar > 0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr > 0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe > 0

There are also two discontinuities in this trend.

Trends in Electron Affinity



- The first occurs between Groups IA and IIA.
  - Added electron must go in *p*-orbital, not *s*-orbital.
  - Electron is farther from nucleus and feels repulsion from *s*-electrons.

Periodic Properties of the Elements

Trends in Electron Affinity

1A	2A	3A	4A	5A	6A	7A	8A
H −73							**He** > 0
Li −60	**Be** > 0	**B** −27	**C** −122	**N** > 0	**O** −141	**F** −328	**Ne** > 0
Na −53	**Mg** > 0	**Al** −43	**Si** −134	**P** −72	**S** −200	**Cl** −349	**Ar** > 0
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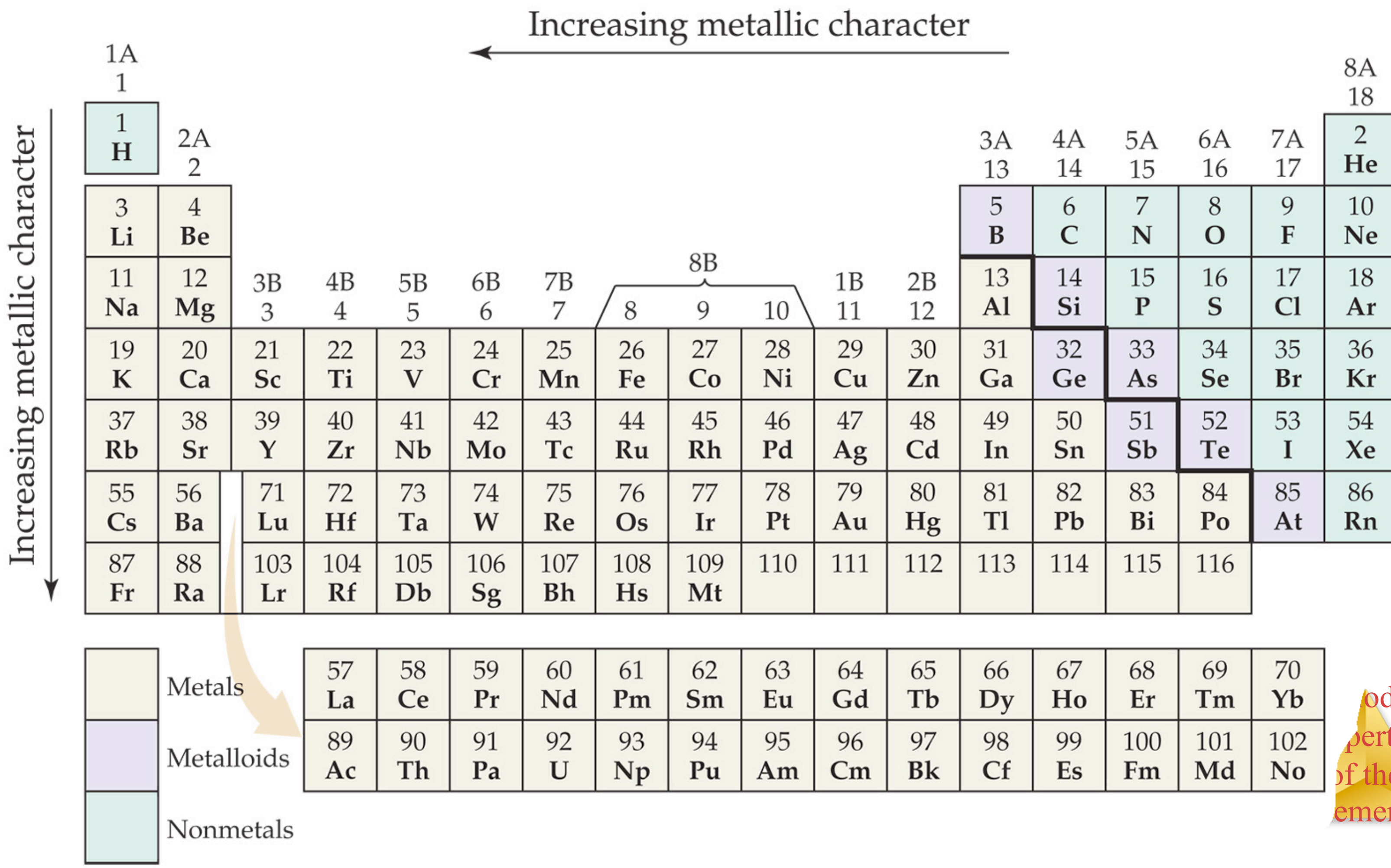
Rb −47	**Sr** −5	**In** −30	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** > 0

- The second occurs between Groups IVA and VA.
  - Group VA has no empty orbitals.
  - Extra electron must go into occupied orbital, creating repulsion.

Properties of Metals, Nonmetals, and Metalloids



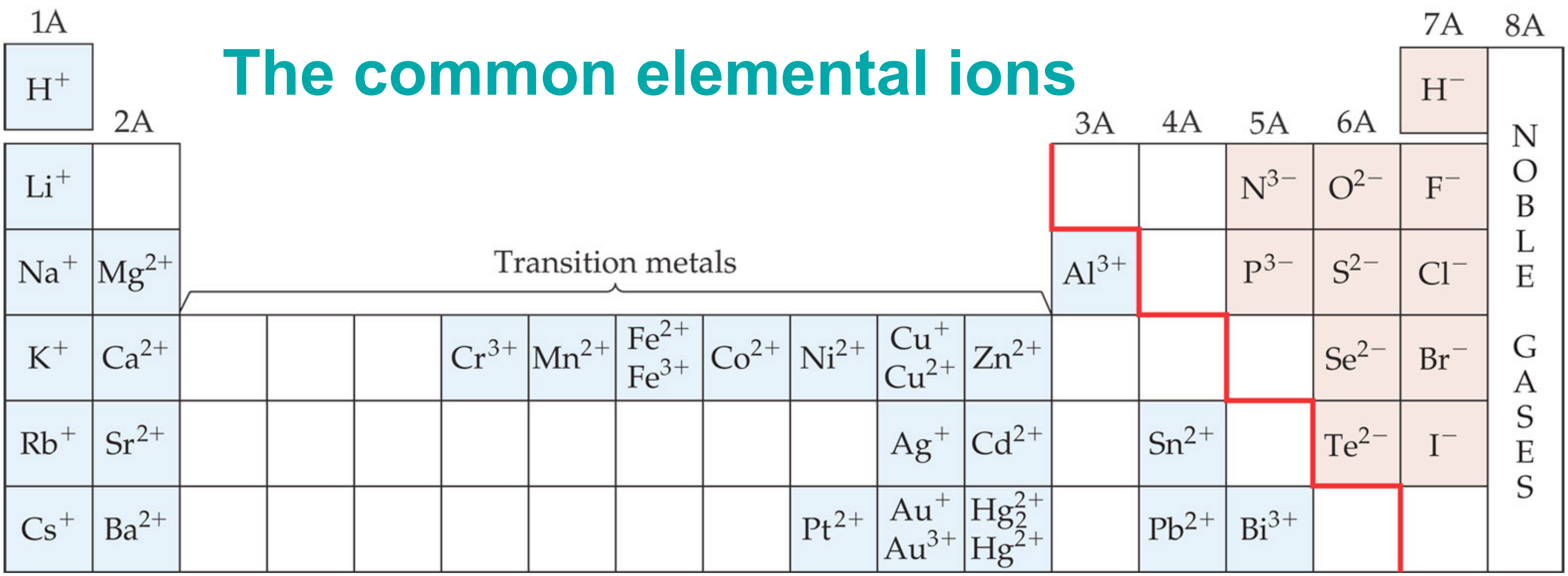
Metals versus Nonmetals

Metals	Nonmetals
Have a shiny luster; various colors, although most are silvery	Do not have a luster; various colors
Solids are malleable and ductile	Solids are usually brittle; some are hard, some are soft
Good conductors of heat and electricity	Poor conductors of heat and electricity
Most metal oxides are ionic solids that are basic	Most nonmetal oxides are molecular substances that form acidic solutions
Tend to form cations in aqueous solution	Tend to form anions or oxyanions in aqueous solution

Differences between metals and nonmetals tend to revolve around these properties.

Metals versus Nonmetals

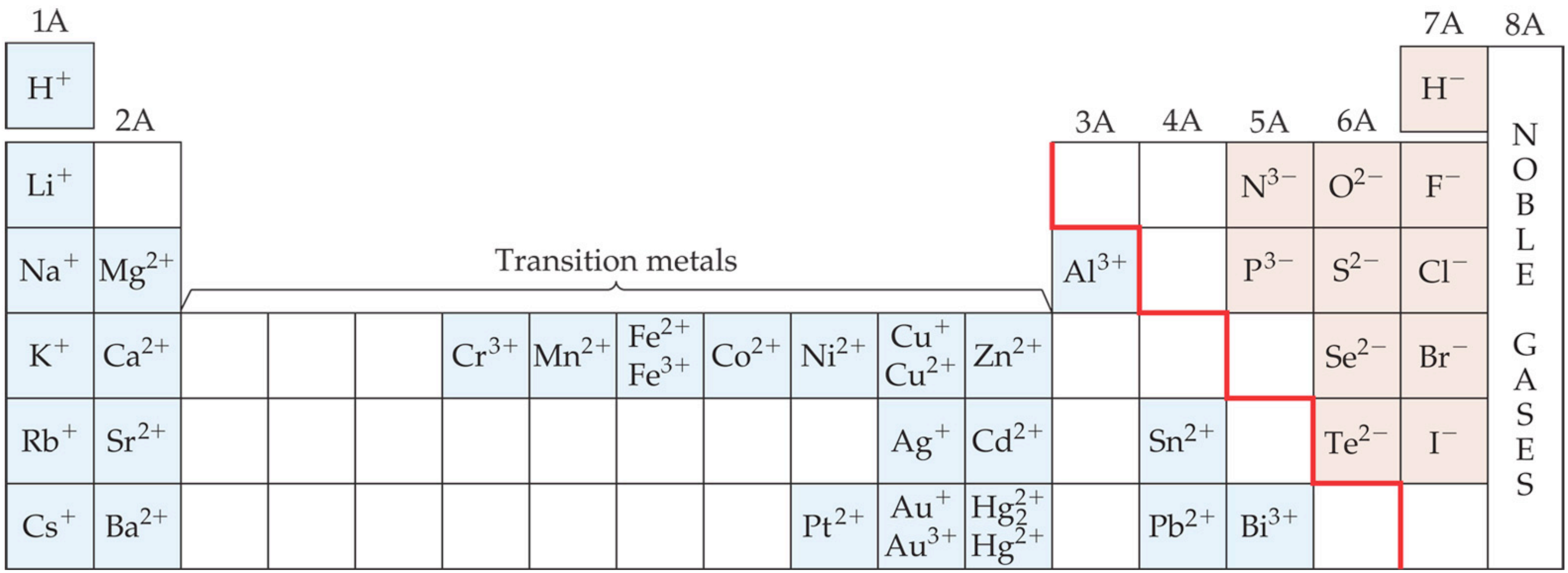
- Metals tend to form cations.
- Nonmetals tend to form anions.



Note ions in s and p world all result from filling or empyting a subshell.

What about the transition metals? What’s going on there?

Transition Metal ions



Note: many have +2 charge.

They actually lose all their ns electrons first!

Mn --> Mn^{2+}: $[Ar]4s^2 3d^5$ ---> $[Ar]3d^5$

Cu --> Cu^+ $[Ar]4s^2 3d^9$ ---> $[Ar]3d^{10}$

Metals

Tend to be lustrous, malleable, ductile, and good conductors of heat and electricity.

Metals

- Compounds formed between metals and nonmetals tend to be ionic.
- Metal oxides tend to be basic.

Nonmetals

- Dull, brittle substances that are poor conductors of heat and electricity.
- Tend to gain electrons in reactions with metals to acquire noble gas configuration.

Nonmetals

- Substances containing only nonmetals are molecular compounds.
- Most nonmetal oxides are acidic.

Periodic Properties of the Elements

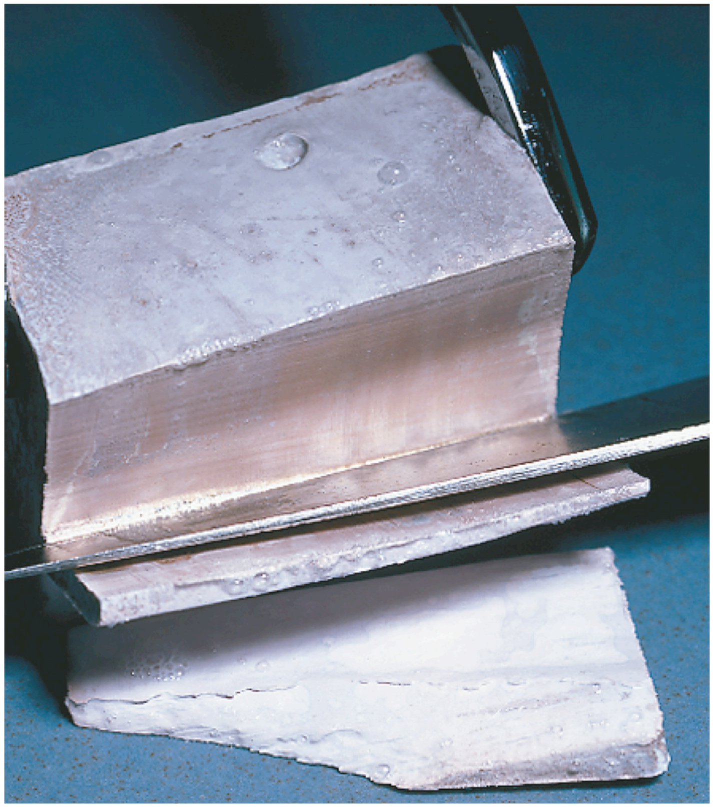
Metalloids

- Have some characteristics of metals, some of nonmetals.
- For instance, silicon looks shiny, but is brittle and fairly poor conductor.

Group Trends

Alkali Metals

- Soft, metallic solids.
- Name comes from Arabic word for ashes.



Periodic Properties of the Elements

Alkali Metals

- Found only as compounds in nature.
- Have low densities and melting points.
- Also have low ionization energies.

Element	Electron Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius (Å)	I_1 (kJ/mol)
Lithium	$[He]2s^1$	181	0.53	1.34	520
Sodium	$[Ne]3s^1$	98	0.97	1.54	496
Potassium	$[Ar]4s^1$	63	0.86	1.96	419
Rubidium	$[Kr]5s^1$	39	1.53	2.11	403
Cesium	$[Xe]6s^1$	28	1.88	2.25	376

Alkali Metals

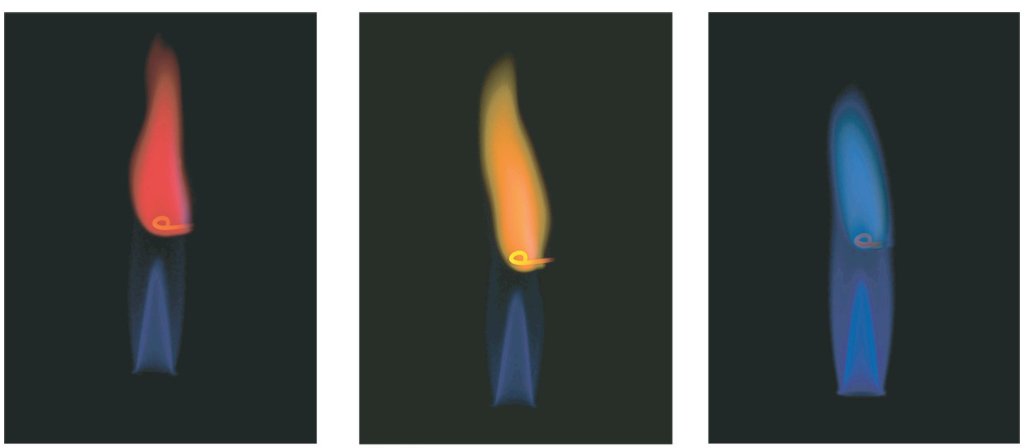
Their reactions with water are famously exothermic.

Alkali Metals

- Alkali metals (except Li) react with oxygen to form peroxides.
- K, Rb, and Cs also form superoxides:

$$K + O_2 \longrightarrow KO_2$$

- Produce bright colors when placed in flame.



Alkaline Earth Metals

Element	Electron Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius (Å)	I_1 (kJ/mol)
Beryllium	$[He]2s^2$	1287	1.85	0.90	899
Magnesium	$[Ne]3s^2$	650	1.74	1.30	738
Calcium	$[Ar]4s^2$	842	1.55	1.74	590
Strontium	$[Kr]5s^2$	777	2.63	1.92	549
Barium	$[Xe]6s^2$	727	3.51	1.98	503

- Have higher densities and melting points than alkali metals.
- Have low ionization energies, but not as low as alkali metals.

Alkaline Earth Metals

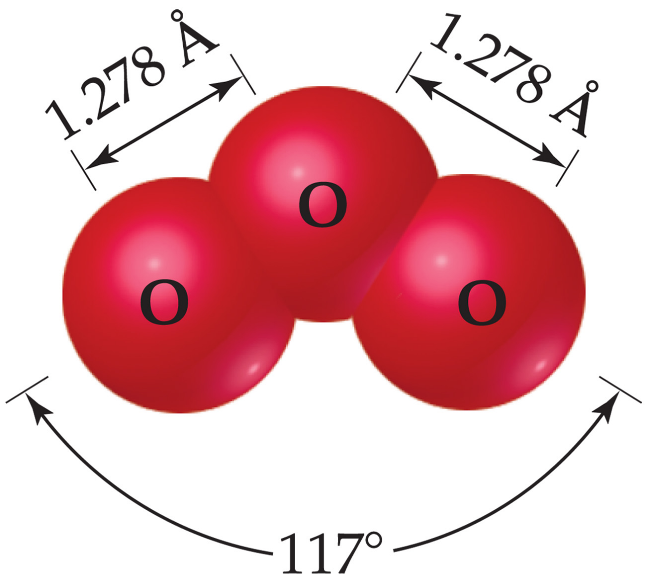
- Be does not react with water, Mg reacts only with steam, but others react readily with water.
- Reactivity tends to increase as go down group.

Group 6A

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ/mol)
Oxygen	$[He]2s^2 2p^4$	−218	1.43 g/L	0.73	1314
Sulfur	$[Ne]3s^2 3p^4$	15	1.96 g/cm^3	1.02	1000
Selenium	$[Ar]3d^{10} 4s^2 4p^4$	221	4.82 g/cm^3	1.16	941
Tellurium	$[Kr]4d^{10} 5s^2 5p^4$	450	6.24 g/cm^3	1.35	869
Polonium	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$	254	9.20 g/cm^3	—	812

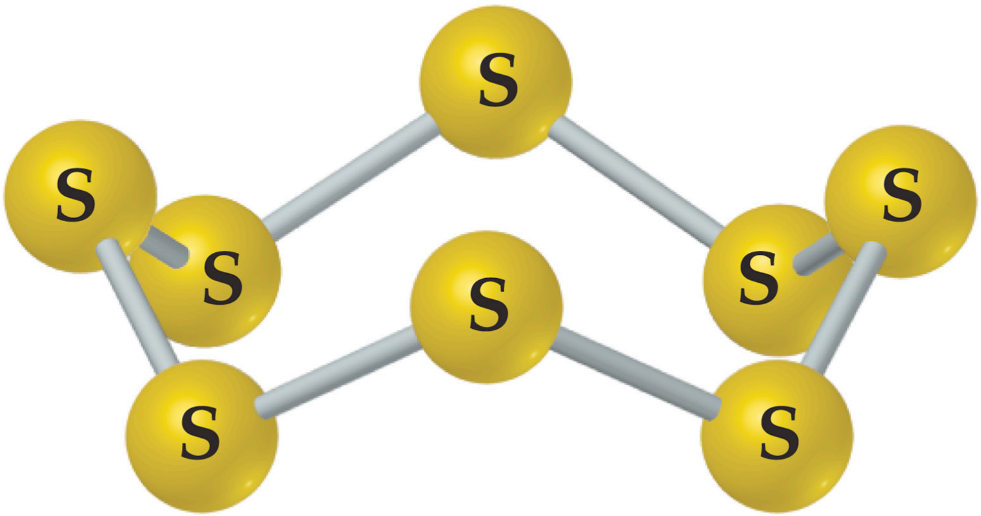
- Oxygen, sulfur, and selenium are nonmetals.
- Tellurium is a metalloid.
- The radioactive polonium is a metal.

Oxygen



- Two allotropes:
  - O_2
  - O_3, ozone
- Three anions:
  - O^{2-}, oxide
  - O_2^{2-}, peroxide
  - O_2^{1-}, superoxide
- Tends to take electrons from other elements (oxidation)

Sulfur



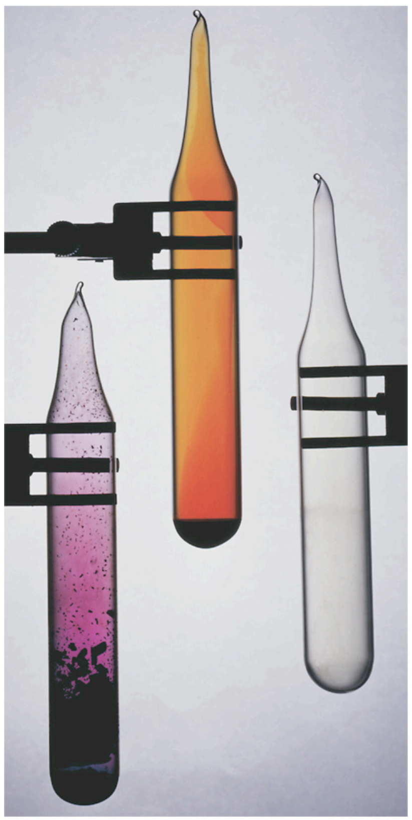
- Weaker oxidizing agent than oxygen.
- Most stable allotrope is S_8, a ringed molecule.

Group VIIA: Halogens

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ/mol)
Fluorine	$[He]2s^2 2p^5$	−220	1.69 g/L	0.71	1681
Chlorine	$[Ne]3s^2 3p^5$	−102	3.21 g/L	0.99	1251
Bromine	$[Ar]3d^{10} 4s^2 4p^5$	−7.3	3.12 g/cm^3	1.14	1140
Iodine	$[Kr]4d^{10} 5s^2 5p^5$	114	4.94 g/cm^3	1.33	1008

- Prototypical nonmetals
- Name comes from the Greek *halos* and *gennao*: “salt formers”

Group VIIA: Halogens



- Large, negative electron affinities
  - Therefore, tend to oxidize other elements easily
- React directly with metals to form metal halides
- Chlorine added to water supplies to serve as disinfectant

Periodic Properties of the Elements

Group VIIIA: Noble Gases

Element	Electron Configuration	Boiling Point (K)	Density (g/L)	Atomic Radius* (Å)	I_1 (kJ/mol)
Helium	$1s^2$	4.2	0.18	0.32	2372
Neon	$[He]2s^22p^6$	27.1	0.90	0.69	2081
Argon	$[Ne]3s^23p^6$	87.3	1.78	0.97	1521
Krypton	$[Ar]3d^{10}4s^24p^6$	120	3.75	1.10	1351
Xenon	$[Kr]4d^{10}5s^25p^6$	165	5.90	1.30	1170
Radon	$[Xe]4f^{14}5d^{10}6s^26p^6$	211	9.73	1.45	1037

*Only the heaviest of the noble-gas elements form chemical compounds. Thus, the atomic radii for the lighter noble-gas elements are estimated values.

- Astronomical ionization energies
- Positive electron affinities
  - Therefore, relatively unreactive
- Monatomic gases

Group VIIIA: Noble Gases

- Xe forms three compounds:
  - XeF_2
  - XeF_4 (at right)
  - XeF_6
- Kr forms only one stable compound:
  - KrF_2
- The unstable HArF was synthesized in 2000.

Exam 2 review:

- Chapter 5, thermochemistry
- Chapter 6, atomic structure
- Chapter 7, periodic trends

Exam 2 review:

- Chapter 5
  - ➢ Heat vs. work, nature of energy
    - potential energy vs. kinetic energy
    - nature of temperature
    - system versus surroundings
  - ➢ 1st law of thermodynamics:
    - ΔE calculations
    - example: Calculate the change in internal energy and whether the process is endo or exo thermic:
      - 100g of water is cooled from 90 °C to 40 °C.
  - ➢ Enthalpy of reaction. Using stoichiometry and enthalpy of reaction to calculate things:
    - example problem:
    - $Ag^+(aq) + Cl^-(aq)$ -------> $AgCl(s)$ $\Delta H = -65.5$ kJ
      a. Calculate ΔH for the formation of 2.5 g of AgCl

Periodic Properties of the Elements

Exam 2 review:

- $Ag^+(aq) + Cl^-(aq)$ -------> $AgCl(s)$ $\Delta H = -65.5$ kJ

  Calculate ΔH for the formation of 2.5 g of AgCl

  MW. 143.319 g/mol (AgCl).

  2.5 g/143.319 g/mol = 0.0174 mole

  0.0174 mol(-65.5 kJ/mol AgCl) = -1.14 kJ

➢ Calorimetry problem:

- example problem:

  10 g of NaOH is dissolved in 100 mL of water in a calorimeter, the temperature changes from 23.6 to 47.4 °C. Calculate ΔH for the process, assume the specific heat of the solution is 4.184 j/°Kg, the same as water.

Chapter 5

q = specific heat(g solution)(ΔT)
q = 4.184j/Kmol(110 g)(26.4 -43.3) = -10953 J
moles NaOH = 10g/40 g = .25 mole
ΔH = -10953 J/.25 mol = -43812 = 40000 J/mol NaOH.

- Hess's law:
  - Given a series of reactions, rearrange to find ΔH for the reaction in question:
  - Example problem:
  - Given the data:
  - $N_2(g) + O_2(g)$ ----> $2NO(g)$ $\Delta H = 180.7$ kJ
  - $2NO(g) + O_2(g)$ -----> $2NO_2$ $\Delta H = -113.1$ kJ
  - $2N_2O(g)$ -----> $2N_2(g) + O_2(g)$ $\Delta H = -163.2$ kJ
  - Calculate: $N_2O(g) + NO_2(g)$ -----> $O_2(g)$
- Enthalpies of formation (the tables of enthalpies of formation):
- $\Sigma\Delta H_{prdts} - \Sigma\Delta H_{reactants} = \Delta H_{reaction}$

Periodic Properties of the Elements

Chapter 5

- Hess's law:
  - Given a series of reactions, rearrange to find ΔH for the reaction in question:
  - Example problem:
  - Given the data:
  - $N_2(g) + O_2(g)$ ----> $2NO(g)$ ΔH =180.7 kJ
  - $2NO(g) + O_2(g)$ -----> $2NO_2$ ΔH = -113.1 kJ
  - $2N_2O(g)$ -----> $2N_2(g) + O_2(g)$ ΔH = -163.2 kJ
  - Calculate: $N_2O(g) + NO_2(g)$ -----> $3NO(g)$

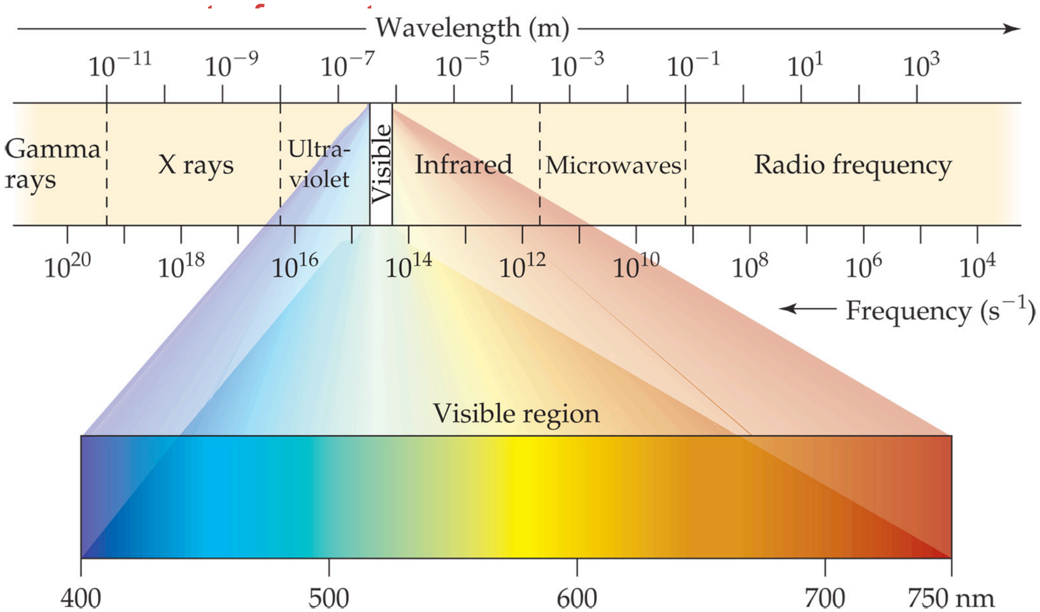
  - NO_2 ---- $NO(g) + 1/2O_2(g)$ 113.1/2
  - $N_2O(g)$ -----> $N_2(g) + 1/2O_2(g)$ ΔH = -163.2/2 kJ
  - $N_2(g) + O_2(g)$ ----> $2NO(g)$ ΔH =180.7 kJ
  - $N_2O(g) + NO_2(g)$ -----> $3NO(g)$ ΔH =155.6 kJ

Chapter 5

- Enthalpies of formation (the tables of enthalpies of formation):
- $\Sigma\Delta H_{prdts} - \Sigma\Delta H_{reactants} = \Delta H_{reaction}$

Chapter 6

- Chapter 6
  - ➢ Characteristics of waves ($v = \lambda\nu$):
    - What is wavelength?
    - What is frequency?
  - ➢ Electromagnetic radiation:
    - $E = h\nu$
    - visible spectrum (ROYGBV)



Periodic Properties of the Elements

Chapter 6

- Chapter 6
  - Characteristics of waves ($v = \lambda\nu$):
  - Black body radiation
  - Photo-electric effect
  - Heisenberg uncertainty: ($\Delta mv\Delta x \geq h$)
  - Line spectra of atoms
  - matter waves (De Brogli)

$$v = \lambda\nu$$

$$\nu = \frac{v}{\lambda}$$

$$E = mv^2 = h\nu = h\frac{v}{\lambda}$$

$$\lambda = \frac{h}{mv}$$

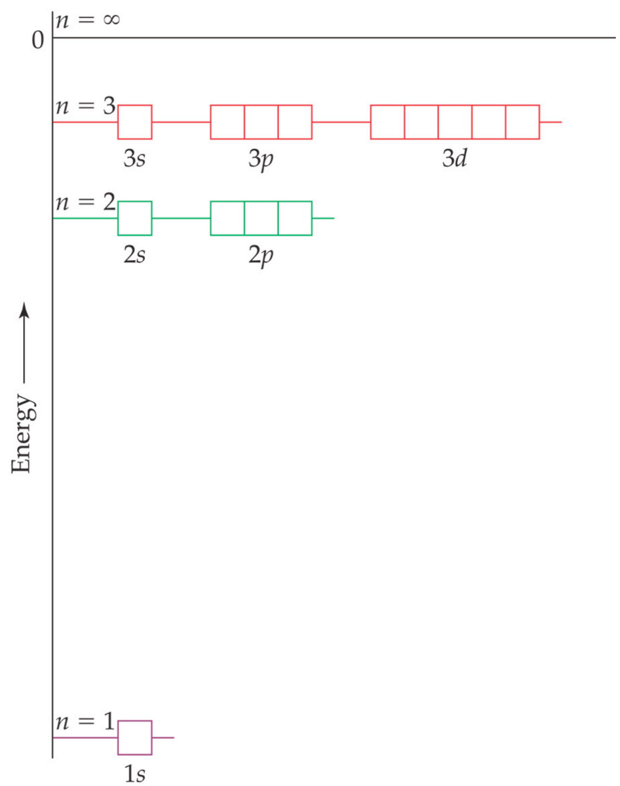
Periodic Properties of the Elements

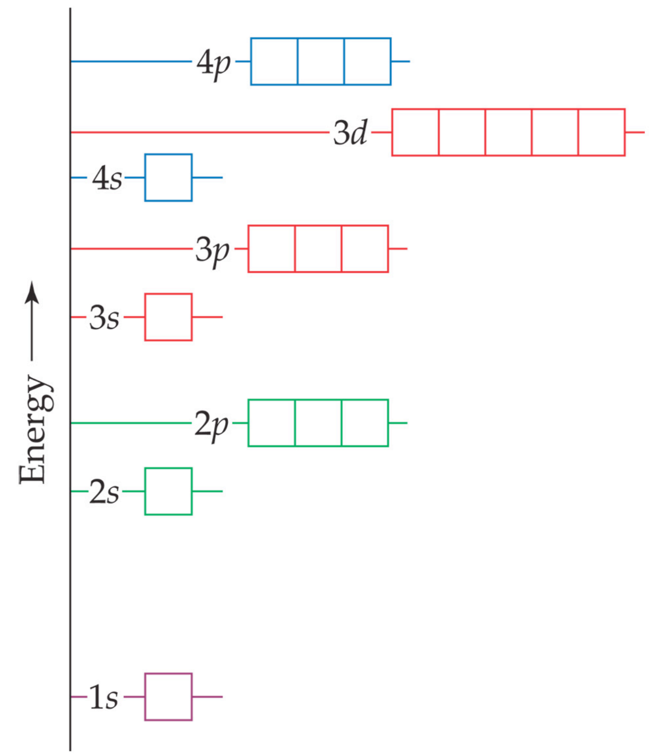
Chapter 6

- Chapter 6
  - ➢ Wavefunctions and quantum mechanics
    - wavefunction vs. probability distribution
    - orbitals and quantum numbers
  - ➢ Quantum numbers
    - what are the four?
      - principle (energy) n = 1,2,3...
      - azimuthal (shape) l = 0,1, 2... n-1
      - magnetic (orientation) m_l = -l,...0,...+l
      - spin (differentiates two electrons in same orbital) (±1/2)
    - naming the l qm:
    - l=0, s, l=1, p, l=2, d, l=3, f
  - ➢ Shapes of orbitals

Chapter 6

- Chapter 6
  - Many electron atoms
  - Energy of orbitals in H versus other atoms with other electrons.

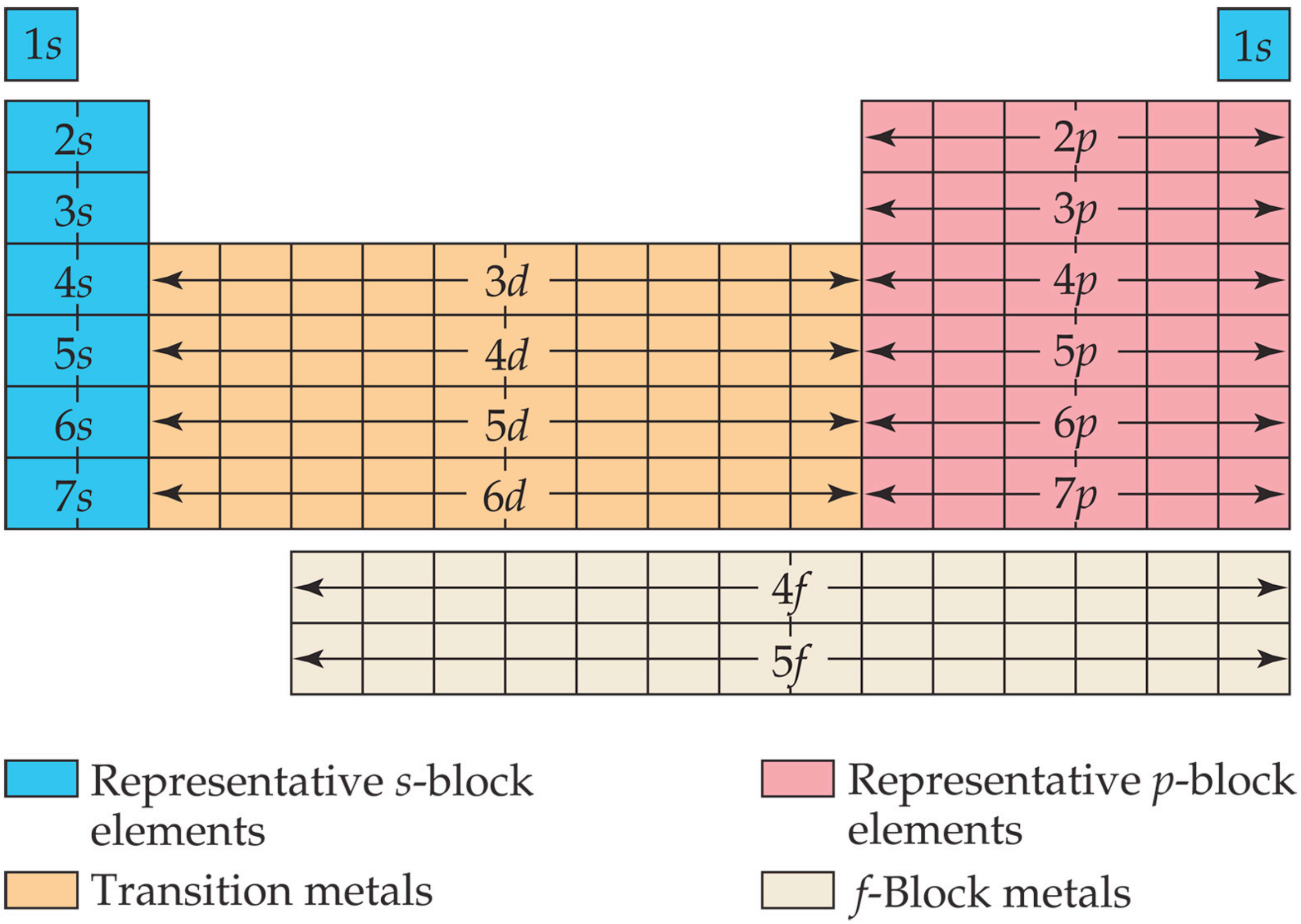


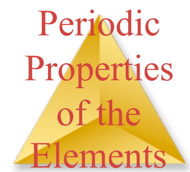


Periodic Properties of the Elements

Chapter 6

- Chapter 6
  - Pauli exclusion principle
  - Hund's rule (don't pair until you have to)
  - Electron configurations





Chapter 7

- Periodic trends
- Effective nuclear charge
- trends in atomic radius
- trends in ion radius
- Ionization energy, trends
- electron affinity, trends.